Measurement and Prediction of Low-Rank Coal Slag Viscosity

Robert C. Streeter,[1] Erle K. Diehl,[2] and Harold H. Schobert[3]

Bituminous Coal Research, Inc., Monroeville, PA 15146
and
Grand Forks Energy Technology Center, Grand Forks, ND 58202

INTRODUCTION

Since 1980, Bituminous Coal Research, Inc., (BCR) has been conducting measurements on the viscosity of western U. S. low-rank coal slags under a contract with the Grand Forks Energy Technology Center (GFETC), U. S. Department of Energy. This work has been motivated by the realization that 1) very few data exist in the literature on the viscosity of low-rank-coal slags; 2) published correlations relating slag viscosity to coal ash composition were derived from work with bituminous-coal slags, and attempts to apply them to data from low-rank coal slags generally have been unsuccessful; and, 3) from a practical standpoint, data on slag rheology are of considerable interest in support of the operation of a slagging fixed-bed lignite gasifier at GFETC. As a matter of related interest, BCR's slag viscometer was originally put into operation in 1976 to obtain data on the slagging properties of coals intended for use in the BI-GAS coal gasification pilot plant at Homer City, Pennsylvania; the BI-GAS process incorporates an entrained-bed, slagging gasifier.

Although the data obtained in these studies have been valuable in interpreting the slagging phenomena observed in the Grand Forks gasifier tests, a more fundamental objective of the current work is to develop correlations that can be used to predict _a priori_ the viscosity behavior of low-rank-coal slags from a knowledge of the ash or slag composition.

EXPERIMENTAL

The slag-viscosity apparatus was assembled for BCR by Theta Industries, Inc. It includes a Lindberg furnace with globar heating elements of silicon carbide, rated for operation at temperatures up to 2732 F (1500 C). The rotating bob viscometer is a Haake RV-2 Rotovisco unit with a DMK 50/500 dual measuring head, which allows adjustment of torque by a factor of 10 (i.e., ranges of 0 to 50 and 0 to 500g-cm).* The torque on the viscometer bob twists a spiral spring inside the measuring head; the angular displacement of the spring is proportional to shear stress, and is converted to an electrical signal that is plotted on an X-Y recorder as a function of the rotational speed of the bob (shear rate). A microprocessor has been incorporated into the original system to provide automatic temperature programming at the rate of about 1°F/min, and stepwise bob rotation from 0 to 64 rpm in increments of 4 rpm.

To simulate conditions existing in the slagging coal gasifier, all tests are carried out in a reducing atmosphere consisting of 20 percent hydrogen and

---

80 percent nitrogen. The gas mixture is injected into the furnace at a flow rate of 500 cc/min through an alumina tube that extends to within 1 inch of the top of the sample crucible.

Although a platinum/rhodium bob was employed initially, some problems were encountered with attack on the bob by molten iron in the slag. In all of the tests discussed herein, the bob was fabricated from 1/2-inch molybdenum bar stock; the bob is approximately 1-inch long with a 30°-angle taper machined on both ends. The top of the bob terminates in a 5/8-inch long, 1/4-inch-diameter shaft which is drilled and tapped to accommodate a 1/8-inch- diameter x 16.5-inch long molybdenum stem. The bob stem is covered by a tubular alumina sleeve to minimize erosion during a test. As originally designed, the viscometer incorporated a universal joint in the measuring head shaft and a Jacobs-type chuck to hold the bob stem. However, this arrangement allowed too much lateral motion of the bob in the slag, and the bob is now attached to the measuring head by a rigid shaft containing three set screws to hold the stem. During a viscosity test, the bob is immersed until the slag just covers its top; the position of the bob can be determined accurately using a depth gauge attached to the measuring head.

In the earlier tests, the slag was melted in crucibles of vitreous carbon, 1-1/4-in. I.D. x 1-3/8-in. high (Atomergic Chemetals Co.). The carbon sample crucible was contained in a larger alumina guard crucible (1-7/8-in. I.D. x 6-in. high) and the annular space between the two crucibles was packed with 60-mesh alundum. The use of carbon crucibles was somewhat influenced by the observation that slag from the gasifier frequently contained particles of devolatilized coal (char), which might be involved in reactions with the molten slag. It soon became evident that iron oxides in the slag were being reduced by reaction with the carbon crucible, as small pools of molten iron invariably settled from the slag during the carbon-crucible tests. With certain coal ashes containing comparatively high amounts of Fe_2O_3, destruction of the carbon crucible was so severe that the portion in contact with the slag virtually disappeared during the viscosity test. Consequently, the carbon crucibles were eventually replaced with high-purity alumina crucibles (McDanel Refractory Co.) of the same dimensions.

Since the alumina crucibles were put into use, metallic iron has only rarely been observed in the slag; if formed at all, the iron usually tends to cling to the top of the bob at the gas/liquid interface. On the other hand, varying degrees of attack on the alumina crucible by the slag have been observed. Generally, dissolution of Al_2O_3 by the slag has been slight, but in a few cases noticeable thinning of the crucible walls has occurred. In addition, with the low-form alumina crucibles, there was a tendency for the slag to overflow the sample crucible and seep into the alundum packing. In a few cases, the slag managed to seep beneath the sample crucible, whereupon subsequent outgassing of the slag actually raised and tilted the sample crucible. To alleviate this problem, high-form (3-in. high) sample crucibles have been employed since September, 1982.

Since measured viscosities will vary depending on the dimensions of and the materials employed for the sample crucible and the rotating bob, measured values are related to absolute viscosities by means of an instrument factor. In these studies, the instrument factor was determined by tests with NBS glass viscosity standards whose viscosities are precisely defined and similar to those of the slags over the temperature range of interest. The instrument factor is related to viscosity by the equation:

Viscosity = Instrument factor x torque reading ÷ bob speed (rpm)

In preparation for a slag-viscosity test, the coal is pulverized to minus-60 mesh and ashed in B&W K-3000 insulating firebrick dishes for 3 hours at 1850 F (1010 C) in a large muffle furnace. This higher-than-normal ashing temperature was chosen after preliminary work showed that sufficient volatiles remained in the ash prepared

175

at the standard "ASTM temperature" of 1382 F (750 C)* to cause severe frothing and foaming during the ash melting process. This difficulty is still experienced to some extent during melting of the high-temperature ash and is believed due to decomposition of residual sulfates and volatilization of alkali-metal oxides in the ash. The coal ash is sieved again at 60 mesh to remove any foreign particles of firebrick, then compressed into pellets 5/8-inch in diameter weighing about 5 grams each. The ash pellets are dropped, one or two at a time, into the previously heated sample crucible through a long quartz tube; a typical coal-ash charge in the high-form alumina crucibles is about 60 to 70 grams.

Viscosity measurements are normally commenced at the highest temperature at which an on-scale reading can be obtained with a bob speed of 64 rpm. The temperature is then decreased slowly (under microprocessor control) and viscosity measurements are taken at approximately half-hour intervals. This "cooling cycle" is continued until the upper limit of the measuring head is approached (typically about 3000 poises**), then the slag is gradually reheated to observe changes in viscosity during a "heating cycle."

Following each test, samples of the solidified slag and high-temperature ash are submitted to GFETC for compositional analyses by X-ray fluorescence and X-ray diffraction techniques. A Kevex Model 0700 energy dispersive X-ray spectrometer is employed for X-ray fluorescence analysis. Samples are ground to minus 60-mesh and pressed into a pellet using either cellulose or lithium tetraborate as a binder. The instrument is calibrated using mixtures of reagent-grade oxides, blended to approximate the relative amounts present in the slag. X-ray diffraction measurements are conducted on minus 325-mesh samples using a Philips 3600 automated X-ray diffractometer. Compound identification is accomplished with the aid of a computer-based index file.

The selection of low-rank coals for these studies was based to some extent on those which had actually been tested or were candidate feedstocks for the GFETC lignite gasifier; in addition, an effort was made to choose samples that would represent a wide range of ash compositions and diverse geographical locations. The coals selected for these viscosity studies are listed in Table 1.‡

RESULTS AND DISCUSSION

Viscosity can be defined as the resistance to flow offered by a fluid and is customarily expressed as the ratio of shear stress to shear rate. The most commonly encountered regime of viscous flow is termed "Newtonian" flow, in which shear stress is a linear function of shear rate (i.e., viscosity is constant at any given shear rate). For Newtonian substances, the dependence of viscosity (η) on

----

* ASTM Method D 3174-73, "Ash in the Analysis Sample of Coal and Coke."

**Throughout this paper, viscosities are given in the more familiar units of poises; the accepted SI unit for viscosity is the Pascal-second, and the conversion is poises x 0.1 = Pa·sec.

‡ In view of the considerable within-seam or within-mine variability of low rank coals, it should be understood that these coal samples are not necessarily representative of the total production of a particular mine.

temperature (T) is exponential, such that a plot of log η vs. T yields a straight line.*   Three other regimes of non-Newtonian behavior are less commonly encountered:

      1.   Pseudoplastic – viscosity decreases with increasing shear rates.

      2.   Plastic – viscosity decreases with increasing shear rates following the appearance of an initial yield stress.

TABLE 1.   SAMPLES SELECTED FOR LOW-RANK COAL VISCOSITY STUDIES

Sample	Rank	Location (State)
1. Indian Head.	Lignite	North Dakota
2. Gascoyne	Lignite	North Dakota
3. Baukol-Noonan	Lignite	North Dakota
4. Beulah	Lignite	North Dakota
5. Colstrip	Sub-bituminous	Montana
6. Decker	Sub-bituminous	Montana
7. Sarpy Creek	Sub-bituminous	Montana
8. Naughton	Sub-bituminous	Montana
9. Big Horn	Sub-bituminous	Wyoming
10. Kemmerer	Sub-bituminous	Wyoming
11. Black Butte	Sub-bituminous	Wyoming
12. Emery	Bituminous (low rank)	Colorado
13. Rockdale	Lignite	Texas
14. Martin Lake	Lignite	Texas
15. Big Brown	Lignite	Texas
16. Atlantic Richfield	Lignite	Texas
17. Burns & McDonnell	Lignite	Alabama

      3.   Thixotropic – viscosity decreases with increasing shear rates and with the duration of the applied shear stress.

In each of these cases, the viscosity varies with shear rate and/or with the period of shear, and the ratio of shear stress to shear rate is customarily designated as "apparent viscosity."

Plots of log η vs. T (°F) for three representative low-rank coal slags are shown in Figure 1.   Curve A for the Black Butte sample illustrates the behavior of a

---

* From purely physico-chemical considerations, log η is proportional to 1/T where T is in °K.   In practice, however, it is often more convenient to plot log η directly vs. temperature in °C, or (as in these studies where engineering conventions were employed in the design and operation of the coal gasifier) in °F.

glassy, siliceous-type slag that exhibits Newtonian properties over a wide tempera-
ture range. In addition, the viscosity behavior is reversible in that viscosities
measured during reheating of the slag (solid circles) are essentially the same as
those determined during the cooling cycle. The type of behavior represented by
Curves B and C is more commonly observed for low-rank coal slags; $\log \eta$ is a linear
function of temperature down to some point, designated as the temperature of criti-
cal viscosity, T_{cv} (as shown for Curve B). Below T_{cv}, the viscosity can increase
quite abruptly (Curve B), or the increase may be somewhat more gradual (Curve C).
Moreover, a "hysteresis" effect appears in the viscosity/temperature curve as the
slag is reheated. This phenomenon is supposedly related to the slow redissolution
of crystals, formed on cooling the slag below T_{cv}.[1] In theory, the viscosity of
the slag on reheating should eventually return to the linear portion of the curve
representing the fully liquid condition. However, as shown by Figure 1, this is not
necessarily achieved experimentally, and the extent of the deviation is believed to
be due to small compositional changes occurring in the melt during the viscosity
determination (to be discussed later). Curve C in Figure 1 includes data points for
two separate viscosity tests with Baukol-Noonan, approximately 6 months apart. As
shown, the repeatability for the cooling curve is quite good; on the other hand,
there is a marked difference in the two curves obtained on reheating the slags, and
subsequent analytical data showed subtle differences in the compositions of the
slags from the two tests.

The straight-line portion of the viscosity/temperature curve is traditionally
designated as the "Newtonian" region of slag behavior, while the area below T_{cv},
where solid species are crystallizing from the melt, is designated as the "plastic"
region. Strictly speaking, a slag can retain Newtonian properties below T_{cv}, and
transition to a non-Newtonian state can be detected only by a change in the shape of
the shear-stress vs. shear-rate curve. As a matter of fact, most of the slags
included in this study actually did show pseudoplastic or thixotropic behavior at
the higher viscosities.

Of the 17 coals listed in Table 1, 13 were tested in carbon crucibles and the
remaining four were tested using alumina crucibles. In addition, the carbon-
crucible test with Baukol-Noonan was repeated, and six of the coals from the carbon-
crucible tests (Big Horn, Decker, Emery, Colstrip, Rockdale, and Burns & McDonnell)
were also selected for alumina-crucible tests. Thus, a total of 24 slag-viscosity
tests provided the data discussed in this paper.

The compositions of the slags from these viscosity tests are listed in Table 2
(compositional data are normalized to 100 percent). Also included are several other
parameters that traditionally have been employed to characterize coal-ash slags. It
should be emphasized that, unless otherwise noted, all calculations discussed herein
were based on <u>slag</u> composition data (as opposed to <u>ash</u> composition data). This was
done primarily for two reasons:

1) As previously noted, reactions with the sample crucible tended to result
in depletion of Fe_2O_3 (carbon-crucible tests) and/or enrichment in Al_2O_3 (alumina-
crucible tests), so that in some cases the composition of the slag was significantly
different from that of the original coal ash. This effect can be seen by comparing
the slag composition data in Table 2 for the carbon- and alumina-crucible tests with
Colstrip, Decker, Big Horn, Emery, Rockdale, and Burns & McDonnell.

2) Results of an independent study, comparing high-temperature ash and slag
compositions for 18 of the 24 viscosity tests, showed that from 80 to 100 percent of
the SO_3 and usually all of the P_2O_5 (if present in the ash) were volatilized during
melting of the ash. Admittedly, P_2O_5 is a minor constituent, and losses of SO_3
could be compensated for by normalizing the analytical data to a sulfur-free basis.
On the other hand, in 11 out of 15 instances (73 percent) where Na_2O was present in
the high-temperature ash, it was volatilized in amounts ranging from 10 to 50 per-
cent of the amount available in the ash. Since the Na_2O content of some ashes

TABLE 2. ANALYSIS OF LOW-RANK-COAL SLAGS PRODUCED IN SLAG VISCOSITY TESTS

Carbon Crucible Tests:

Sample	Slag Composition, Weight Percent										Base/ Acid Ratio (1)	Silica Ratio (2)	SiO_2/ Al_2O_3 Ratio	Lignite Factor (3)
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3				
Gascoyne	42.4	14.8	3.1	1.4	0.0	25.7	8.2	3.7	0.1	0.2	0.70	53.4	2.86	10.9
Baukol-Noonan 1	41.4	19.2	1.0	2.3	0.0	21.8	4.3	7.7	0.6	1.2	0.56	60.4	2.16	26.1
Baukol-Noonan 2	39.3	19.7	4.5	1.7	0.0	18.3	4.4	9.9	0.6	1.1	0.62	59.1	1.99	5.0
Colstrip	45.0	23.9	2.1	1.8	0.0	20.6	5.9	0.1	0.1	0.4	0.41	61.1	1.88	12.6
Decker	38.4	20.0	6.5	2.1	0.0	18.7	4.2	8.6	0.3	0.9	0.63	56.6	1.92	3.5
Sarpy Creek	44.2	27.4	1.9	1.1	0.0	18.3	4.0	1.2	1.2	0.3	0.37	64.6	1.61	11.7
Naughton	63.5	17.8	5.5	0.8	0.2	6.7	3.6	0.0	1.6	0.1	0.21	80.1	3.57	1.9
Big Horn	27.1	28.6	11.4	1.5	0.7	16.3	6.9	5.0	0.5	1.8	0.70	43.9	0.95	2.0
Kemmerer	59.6	13.3	0.9	0.9	0.0	15.5	7.7	0.8	0.6	0.1	0.35	71.2	4.48	25.8
Black Butte	53.9	18.3	6.0	1.3	0.0	11.7	4.2	4.0	0.3	0.0	0.36	71.1	2.94	2.6
Emery	40.2	21.4	9.1	1.1	0.1	16.9	5.5	2.9	0.2	2.0	0.55	56.1	1.88	2.5
Rockdale	42.9	24.0	2.4	2.0	0.0	23.8	3.9	0.0	0.5	0.3	0.44	58.8	1.79	11.5
Atlantic Richfield	40.6	15.8	2.7	2.0	0.1	29.4	6.7	2.0	0.3	0.2	0.70	51.1	2.57	13.4
Burns&McDonnell	47.0	26.1	12.7	0.8	0.0	6.6	3.7	0.0	2.2	0.5	0.34	67.1	1.80	0.8

179

TABLE 2. ANALYSIS OF LOW-RANK-COAL SLAGS PRODUCED IN SLAG VISCOSITY TESTS (Continued)

Alumina Crucible Tests:

Sample	Slag Composition, Weight Percent										Base/Acid Ratio (1)	Silica Ratio (2)	SiO$_2$/Al$_2$O$_3$ Ratio	Lignite Factor (3)
	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	P$_2$O$_5$	CaO	MgO	Na$_2$O	K$_2$O	SO$_3$				
Indian Head	20.0	36.7	12.5	0.6	0.0	17.0	7.1	5.4	0.1	0.0	0.73	35.3	0.54	1.9
Beulah (high sodium)	24.2	33.6	14.0	0.9	0.0	14.4	4.3	8.1	0.2	0.3	0.70	42.5	0.72	1.3
Colstrip	38.0	28.1	11.2	1.5	0.0	17.1	3.9	0.0	0.1	0.0	0.48	54.1	1.35	1.9
Decker	36.1	23.0	8.8	2.1	0.0	18.2	3.8	7.5	0.2	0.0	0.63	54.0	1.57	2.5
Big Horn	30.2	24.7	13.6	1.8	0.8	18.1	5.5	4.5	0.5	0.1	0.74	44.8	1.22	1.7
Emery	44.2	24.7	7.4	1.4	0.0	15.1	4.1	2.6	0.2	0.0	0.42	62.4	1.79	2.6
Rockdale	38.5	27.5	8.9	1.7	0.0	20.0	2.7	0.0	0.4	0.0	0.47	54.9	1.40	2.6
Martin Lake	39.0	22.4	11.6	1.1	0.0	22.4	2.5	0.0	1.0	0.1	0.60	51.6	1.74	2.1
Big Brown	(analytical data for slag not yet available)													
Burns&McDonnell	45.7	23.1	18.9	0.8	0.0	6.0	2.8	0.0	2.0	0.2	0.43	62.3	1.98	0.5

(1) Base/Acid Ratio = (Fe$_2$O$_3$ + CaO + MgO + Na$_2$O + K$_2$O)/(SiO$_2$ + Al$_2$O$_3$ + TiO$_2$) (Ref. 2)

(2) Silica Ratio = 100 SiO$_2$/(SiO$_2$ + "Fe$_2$O$_3$" + CaO + MgO) where "Fe$_2$O$_3$" = (Fe$_2$O$_3$ + 1.11 FeO + 1.43 Fe) (Ref. 3)

(3) Lignite Factor = (CaO + MgO)/Fe$_2$O$_3$ (Ref. 2). Theoretically, Σ(CaO + MgO + Fe$_2$O$_3$) must be greater than 20% and the lignite factor must be greater than 1.0 for the ash (slag) to be considered a low-rank-coal type; the Burns&McDonnell sample is an obvious exception to this rule.

180

ranged up to 10 percent, it is probable that volatilization of this constituent would have an effect on the slag viscosity.

The data in Table 2 illustrate the wide variability in concentrations of low-rank-coal slag constituents. This variability is reflected further by Table 3, where the ranges in slag compositions encountered during these studies (Table 2) are compared with the ash composition of an "average" bituminous coal (SO_3-free basis).(4) Especially noteworthy are the higher concentrations of alkaline-earth and alkali metal oxides in the low-rank coal slags.

The experimental viscosity data from these studies are summarized in Table 4. The two viscosity values shown for each sample, corresponding to specific melt temperatures, are sufficient to approximate the linear ("Newtonian") portion of the log η vs. T curve obtained during the cooling cycle. In addition, values for T_{cv} (when observable) and ash fusibility (reducing atmosphere) for the high-temperature ash (HTA) are included for comparison.

Slag Viscosity/Composition Correlations

Several attempts have been made in the past to define the linear portion of the viscosity/temperature curve based on the composition of the coal ash. In the mid-1960's, workers at the British Coal Utilization Research Association (BCURA) developed two such correlations based on work with British (bituminous) coals, now generally referred to as the Watt-Fereday(5) and "S^2"(3) correlations.* The Watt-Fereday correlation is based on results of 276 determinations of slag viscosity using 113 different ash compositions prepared by blending British coal ashes. Unfortunately, attempts to apply this correlation to low-rank coal slags, using either ash- or slag-composition data, have been generally unsuccessful. This is illustrated by Figure 2, in which the viscosity/temperature cooling curves for two Texas lignites, Big Brown and Martin Lake, are plotted. The corresponding Watt-Fereday correlation lines are based on the (750 C ASTM) ash-composition data. As indicated by Figure 2, the ash compositions and ash fusion temperatures of these two coals are very similar. However, the viscosity predicted by the Watt-Fereday correlation for Big Brown was higher than that observed experimentally, while for Martin Lake the Watt-Fereday equation under-predicted the actual viscosity.

Among the possible reasons why these predictive equations fail for low-rank coals are the following:

1. Ash constituents may fall outside the range of those in most bituminous coals (Table 3).

2. The BCURA predictive equations are based on ash analyses. As discussed earlier, significant losses of certain elements may occur as the ash from low-rank coals is heated to the melting point.

3. Sulfur retention is more prevalent in low-rank coal ashes, due to the generally higher calcium contents. Some of the slags from these viscosity studies retained up to 2 percent SO_3 (Table 2), even after being heated above 2600 F (1427 C).

4. In lignites, some 30 to 50 percent of the ash-forming constituents can consist of cations attached to the organic matter in ion-exchangeable form on carboxyl groups or as chelate complexes, rather than being present as distinct mineralogical species.(6)

---

* Details of the viscosity/composition correlations are presented in Appendix 1.

TABLE 3. COMPARISON OF "AVERAGE" BITUMINOUS COAL
ASH COMPOSITION WITH LOW-RANK-COAL SLAG COMPOSITIONS

Constituent	Range in Low-Rank-Coal Slags from Viscosity Studies, Wt. Percent*	"Average" Bituminous Coal Ash (SO_3-free), Wt. Percent
SiO_2	20.0 - 63.5	48.1
Al_2O_3	13.3 - 36.7	24.9
Fe_2O_3	0.9 - 18.9	14.9
TiO_2	0.6 - 2.3	1.1
CaO	6.0 - 29.4	6.6
MgO	2.5 - 8.2	1.7
Na_2O	0.0 - 9.9	1.2
K_2O	0.1 - 2.0	1.5

* From data in Table 2.

TABLE 4. EXPERIMENTAL DATA FROM LOW-RANK-COAL SLAG VISCOSITY STUDIES

Carbon Crucible Tests: Sample	Temperature Range of Viscosity Measurements (Melt Temp., °F)	Measured Viscosity at Indicated Temperature		T_{cv}, °F (Approx.)	HTA Fusion Temperatures, °F		
		η, poises	T, °F		Initial Deformation	Softening (Spherical)	Fluid
Gascoyne	2510 - 2145	25 / 102	2458 / 2237	2180	2000	2080	2120
Baukol-Noonan 1	2480 - 2090	41 / 482	2480 / 2133	2125	2000	2040	2100
Baukol-Noonan 2	2340 - 2100	93 / 548	2343 / 2128	2125	2000	2040	2100
Colstrip	2560 - 2320	39 / 102	2557 / 2463	2450	2100	2180	2280
Decker	2350 - 2110	50 / 289	2346 / 2147	2145	2020	2060	2120
Sarpy Creek	2700 - 2460	56 / 220	2697 / 2491	2490	2000	2080	2140
Naughton	2730 - 2550	979 / 3375	2731 / 2553	none	2100	2200	2320
Big Horn	2490 - 2225	93 / 325	2407 / 2272	2270	2060	2100	2140
Kemmerer	2640 - 2340	88 / 589	2637 / 2413	2375*	2100	2160	2300
Black Butte	2690 - 2290	140 / 3375	2688 / 2294	none	2080	2120	2200
Emery	2620 - 2270	98 / 422	2548 / 2354	2325*	2060	2120	2260
Rockdale	2680 - 2440	26 / 105	2681 / 2481	2475	2080	2160	2220
Atlantic Richfield	2400 - 2125	27 / 172	2396 / 2183	2175	2040	2100	2140
Burns & McDonnell	2690 - 2370	94 / 272	2690 / 2535	2500*	2000	2080	2260

Alumina Crucible Tests: Sample	Temperature Range of Viscosity Measurements (Melt Temp., °F)	Measured Viscosity at Indicated Temperature		T_{cv}, °F (Approx.)	HTA Fusion Temperatures, °F		
		η, poises	T, °F		Initial Deformation	Softening (Spherical)	Fluid
Indian Head	2650 – 2350	48 82	2594 2508	2500*	2100	2200	2320
Beulah (high sodium)	2640 – 2270	38 340	2597 2380	2330*	2060	2140	2220
Colstrip	2650 – 2360	18 34	2653 2520	2470*	2100	2180	2280
Decker	2290 – 2090	69 237	2286 2146	2145	2020	2060	2120
Big Horn	2390 – 2110	90 289	2331 2177	2175	2060	2100	2140
Emery	2560 – 2280	53 114	2564 2441	2420	2060	2120	2260
Rockdale	2620 – 2440	25 36	2617 2553	2525	2080	2160	2220
Martin Lake	2680 – 2260	43 635	2679 2322	2320	2100	2140	2200
Big Brown	2530 – 2300	24 59	2530 2385	2350	2080	2120	2180
Burns & McDonnell	2700 – 2150	40 242	2698 2402	2300*	2000	2080	2260

*T_{cv} not well defined.

The Watt-Fereday equation is approximately a linear equation of the form

$$\log \eta = m \cdot f(T) + c \tag{1}$$

where m is normally positive and c is negative. Revised values for the slope (m´) and intercept (c´) can be calculated based on the experimental data for the low-rank coals to obtain a good fit to the Watt-Fereday equation. However, for 20 of 23 tests (87 percent) the value of m´ was larger than that predicted by the conventional Watt-Fereday equation; similarly, absolute values of c´ were also larger for 16 of 23 tests (70 percent). Since the intercept is negative, these two effects should tend to offset each other, resulting in little change in the value of log η. In reality, the net result tended to be a larger value for log η, such that observed viscosities were higher than predicted viscosities in 18 of the 23 tests (78 percent). Thus, these studies indicate that the viscosities of low-rank coal slags are generally higher than those of slags derived from bituminous coals.

Attempts were made to correlate the experimental values of m´ and c´ with slag composition data (Table 2) using multiple linear regression analysis. These attempts were generally unsuccessful, although for the carbon-crucible tests, the correlation of m´ with Na_2O content was significant at the 99.5 percent confidence level, and for the alumina-crucible tests, Na_2O was ranked second in correlations for both m´ and c´ (even though not statistically significant). These findings suggest that the role of Na_2O in low-rank-coal slags may be more important than previously realized.

Other combinations of variables, including those listed in Table 2, were employed in efforts to derive empirical correlations with slag viscosity, but again without much success. In addition, the BCURA S^2 correlation[3] and a modified form of the Watt-Fereday correlation developed at the National Bureau of Standards[7] were tested. Of the 23 viscosity tests for which slag composition data are available, the NBS correlation gave a good fit to the experimental data in only two cases, while the S^2 correlation applied in only one case. Generally, the NBS and S^2 calculations gave higher viscosities than those predicted from the conventional Watt-Fereday treatment; the S^2 values were larger for 22 (96 percent) of the 23 tests, and the NBS values were larger for 19 (83 percent) of the tests. On the other hand, all three correlations had a tendency to underestimate the slag viscosity, as observed viscosities were greater than those estimated by any of the three predictive methods in 14 (61 percent) of the tests. Consequently, we conclude that the BCURA methods (or the NBS modification thereof) are generally unsatisfactory for estimating the viscosities of low-rank coal slags.

More recently, two correlations have appeared in the literature that were developed in France in studies with metallurgical (steel making) slags: the IRSID correlation, published by Riboud et al.,[8] and the Urbain correlation.[9] These two correlations are conceptually more appealing because:

• Unlike the BCURA correlations, which are based on the Arrhenius form of the viscosity equation

$$\eta = A \exp(E/RT), \tag{2}$$

the IRSID and Urbain correlations are based on the Frenkel relation

$$\eta = AT \exp(B/T) \tag{3}$$

which, according to the authors, is the preferred form.

• All slag constituents are included, rather than just the five major oxides.

• Slag constituents are expressed as mole fractions instead of weight percentages.

• The Urbain correlation is based on the SiO_2-Al_2O_3-CaO pseudo ternary phase diagram, and these three constituents usually predominate in low-rank coal slags.

However, there is a slight complication in that these correlations assume the oxidation state of iron in the slag is known. Since this information is not currently available for the low-rank-coal slags, and because all tests were in a reducing atmosphere, for computational purposes it was tentatively assumed that all iron was in the form of FeO.*

On this basis, the IRSID correlation gave a reasonably good fit to the experimental data (within 20 percent) for three of the 23 viscosity tests. Unlike the BCURA correlations, which tended to give consistently low results, the error in the IRSID correlation tended to be random; predicted viscosities were too high in 11 cases and too low in nine cases.

The Urbain correlation was acceptable for six tests, too high in seven instances, and too low in 10 instances. Furthermore, even though the Urbain correlation was unsatisfactory for 17 tests, compared with the IRSID correlation, the predicted viscosities were closer to the actual values in 10 instances. Of all the correlations tested (including the BCURA correlations), the Urbain correlation was judged to give the closest agreement to the actual viscosities in seven of the 23 tests; among the remaining 16 tests, the Urbain correlation was judged second-best for nine.

Since the Urbain method appeared to give a fair-to-good correlation for nearly two-thirds of the viscosity tests, efforts were directed toward modifying this procedure with the goal of optimizing the fit to the experimental data. The logarithmic form of the Urbain equation is

$$\ln \eta = \ln A + \ln T + 10^3 B/T \quad (\text{T in } °K) \tag{4}$$

where B is a parameter defined by the composition of the slag and A is a function of B. The equation can be "forced" to fit the experimental data by adding a fourth term

$$\ln \eta = \ln A + \ln T + 10^3 B/T + \Delta \tag{5}$$

where Δ is the difference (either positive or negative) between the actual and computed (by equation 4) values of $\ln \eta$. Since $\ln \eta$ is a linear function of temperature above T_{cv}, Δ will also be a linear function of temperature:

$$\Delta = mT \ (°K) + b \tag{6}$$

Thus, for each slag, values for m and b can be derived from the experimental viscosity data which uniquely define the linear portion of the viscosity/temperature curve by means of equation 5. The process then becomes one of correlating the variables m and b with some particular property of the slag.

It was found that, to a first approximation, b could be correlated with m by means of the expression

$$b = -1.6870(10^3 m) + 0.2343 \tag{7}$$

---

* Some very limited data from Mössbauer spectroscopy analysis indicate the presence of ferrous silicate phases in the slags. In cases where metallic iron was formed as a separate phase, it was normally removed before the slag sample was subjected to X-ray analysis.

with a correlation coefficient R = -0.988 for all 23 viscosity tests. The process
was then reduced to finding a correlation for the variable m. Unfortunately, how-
ever, although a number of such correlations were attempted based on individual slag
constituents and combinations thereof, no single correlation was found that satis-
fied the data from all the viscosity tests.

As a further refinement, the slags were subdivided into three groups based on
the magnitude of the parameter B in the Urbain equation (equation 4). The magnitude
of this parameter is related to the location of the slag composition in the
SiO_2-Al_2O_3-CaO ternary phase diagram, and it is proportional to the silica content
of the slag. Thus, with certain borderline cases, the three subgroups correspond
roughly to "high-silica," "intermediate-silica," and "low-silica" slags.

The "high-silica" group included the five tests with Naughton, Burns &
McDonnell, Black Butte, and Kemmerer (B>28), and a fair correlation (R = -0.971) was
found for m of the form

$$10^3m = -1.7264F + 8.4404 \qquad (8)$$

where $F = SiO_2/(CaO + MgO + Na_2O + K_2O)$ and slag components are in mole fractions.
With this correlation, calculated viscosities were within 10 percent (very good) of
actual viscosities for one test, within 30 percent (acceptable) for two other tests,
and within 60 percent (marginally acceptable) for the 4th of five tests. Similarly,
for the "intermediate-silica" slags (Colstrip, Rockdale, Emery, Sarpy Creek, and
Martin Lake; B = 24 to 28), an expression similar to equation 8 was found. In this
case, however, the correlating variable (F) appeared to be the product of the Urbain
parameter B times the sum of the mole fractions of Al_2O_3 and FeO. For the eight
viscosity tests in this group, the modified correlation was very good for two,
acceptable for two others, and marginally acceptable for two more. For the "low-
silica" slags (Gascoyne, Baukol-Noonan, Indian Head, Big Horn, Decker, Atlantic
Richfield, and Beulah; B <24), the correlating variable chosen was $CaO/(CaO + MgO + Na_2O + K_2O)$ (mole fractions), although the correlation was less satisfactory, being
very good for two tests, acceptable for two others, and marginally acceptable for
two more, out of 10 tests. The equations developed for the modified Urbain corre-
lations are summarized below, and viscosities calculated using the various correla-
tions are compared with measured viscosities in Table 5.

High-Silica Slags:

$$b = -1.7137(10^3m) + 0.0509 \quad (R = -0.990 \text{ for 5 of 5 data points})$$

$$10^3m = -1.7264F + 8.4404 \qquad (R = -0.971 \text{ for 5 of 5 data points})$$

where $F = SiO_2/(CaO + MgO + Na_2O + K_2O)$, mole fractions.

Intermediate-Silica Slags:

$$b = -2.0356(10^3m) + 1.1094 \quad (R = -0.998 \text{ for 7 of 8 data points})$$

$$10^3m = -1.3101F' + 9.9279 \qquad (R = -0.982 \text{ for 5 of 8 data points})$$

where $F' = B(\text{eqn. 4}) \times (Al_2O_3 + FeO)$

187

TABLE 5. OBSERVED AND CALCULATED VISCOSITIES FOR LOW-RANK-COAL SLAGS

Carbon Crucible Tests:

Sample	Temp., °F	Observed Viscosity, poises	Viscosity (poises) Calculated from Predictive Correlations					
			Modified Urbain	Conventional Urbain	IRSID	Watt-Fereday	NBS-Modified Watt-Fereday	BCURA S^2
Gascoyne	2458 / 2237	25 / 102	25 / 105	33 / 93	31 / 103	20 / 80	44 / 157	44 / 190
Baukol-Noonan 1	2480 / 2133	41 / 482	40 / 524	48 / 296	56 / 500	54 / 822	101 / 1523	87 / 945
Baukol-Noonan 2	2343 / 2128	93 / 548	273 / 2276	83 / 269	91 / 371	119 / 738	197 / 1220	176 / 833
Colstrip	2557 / 2463	39 / 102	117 / 233	80 / 128	133 / 242	37 / 64	67 / 118	60 / 105
Decker	2346 / 2147	50 / 289	158 / 911	78 / 228	94 / 346	84 / 414	134 / 651	129 / 536
Sarpy Creek	2697 / 2491	56 / 220	45 / 177	60 / 169	83 / 318	27 / 86	43 / 144	44 / 139
Naughton	2731 / 2553	979 / 3375	611 / 2018	667 / 2110	264 / 777	262 / 817	180 / 587	365 / 963
Big Horn	2407 / 2272	93 / 325	130 / 477	44 / 85	67 / 172	10 / 22	22 / 48	23 / 57
Kemmerer	2637 / 2413	88 / 589	118 / 753	121 / 415	98 / 341	116 / 514	149 / 649	151 / 566
Black Butte	2688 / 2294	140 / 3375	94 / 2385	109 / 1059	90 / 1023	94 / 1494	91 / 1544	113 / 1227
Emery	2548 / 2354	98 / 422	44 / 157	42 / 107	61 / 201	24 / 74	37 / 113	34 / 114
Rockdale	2681 / 2481	26 / 105	41 / 165	38 / 97	55 / 185	16 / 44	29 / 82	23 / 70
Atlantic Richfield	2396 / 2183	27 / 172	12 / 28	42 / 120	47 / 163	20 / 82	46 / 165	50 / 222
Burns & McDonnell	2690 / 2535	94 / 272	105 / 304	119 / 272	160 / 448	54 / 129	47 / 118	64 / 151

TABLE 5. OBSERVED AND CALCULATED VISCOSITIES FOR LOW-RANK-COAL SLAGS (Continued)

Alumina Crucible Tests:

Sample	Temp., °F	Observed Viscosity, poises	Viscosity (poises) Calculated from Predictive Correlations					
			Modified Urbain	Conventional Urbain	IRSID	Watt-Fereday	NBS-Modified Watt-Fereday	BCURA S²
Indian Head	2594	48	24	21	19	2	5	4
	2508	82	52	30	34	3	7	6
Beulah (high sodium)	2597	38	31	24	24	5	8	7
	2380	340	249	65	103	13	25	24
Colstrip	2653	18	16	43	70	12	18	15
	2520	34	30	80	166	23	35	32
Decker	2286	69	214	124	180	91	145	143
	2146	237	690	273	488	283	451	399
Big Horn	2331	90	101	67	91	17	31	41
	2177	289	344	150	268	48	81	124
Emery	2564	53	66	96	138	51	68	68
	2441	114	145	183	309	107	146	142
Rockdale	2617	25	24	50	87	16	24	20
	2553	36	34	68	131	21	33	29
Martin Lake	2679	43	16	27	31	9	13	10
	2322	635	135	148	274	54	77	87
Burns & McDonnell	2698	40	73	82	97	38	28	32
	2402	242	491	401	670	202	156	178

Low-Silica Slags:

$$b = -1.8244(10^3 m) + 0.9416 \quad (R = -0.999 \text{ for 6 of 10 data points})$$

$$10^3 m = -55.3649 F'' + 37.9186 \quad (R = -0.970 \text{ for 7 of 10 data points})$$

where $F'' = CaO/(CaO + MgO + Na_2O + K_2O)$, mole fractions.

The nature of the "F" terms in the modified Urbain correlations is of interest. Urbain categorizes the constituents of silicate melts as "glass formers" (SiO_2, P_2O_5), "modifiers" (CaO, MgO, Na_2O, K_2O) and "amphoterics" (Al_2O_3, Fe_2O_3) which can act either as glass formers or modifiers. The correlating term for high-silica slags is the ratio of SiO_2 to modifiers, suggesting that, for these slags, the silica content of the slag is the dominating factor. On the other hand, for low-silica slags the correlating term is the ratio of CaO to modifiers, which implies that the amount of CaO relative to total modifiers in the slag is a critical factor. For intermediate-silica slags, the correlating term involves the "amphoterics," suggesting that the role of these constituents becomes more important when the nature of the slag cannot be well defined by its silica content.

SUMMARY AND FUTURE WORK

Data from 23 low-rank coal slag viscosity determinations have been employed in attempts to correlate the linear portion of the log viscosity vs. temperature curve with five published empirical correlations for silicate slags. Of these five correlations, one developed by Urbain for metallurgical slags appeared to give a reasonable fit to the experimental data for nearly two-thirds of the viscosity tests. When the slags were subdivided into three groups, based on a parameter of the Urbain equation that is roughly proportional to silica content, it was possible to derive modified forms of the Urbain equation that gave acceptable correlations (within 30 percent) for 11 of the viscosity tests. Of the remaining 12 tests, the modified correlations were marginally acceptable (within 60 percent) in five cases.

Efforts are still being made to refine these empirical correlations and, in particular, to understand the reasons why certain slags fail to fit the correlations. The ultimate objective is to interpret slag rheological behavior in terms of specific phases present in the slag, to the extent that such phases can be identified and quantified.

ACKNOWLEDGMENTS

REFERENCES

1. Watt, J. D. and F. Fereday, "The flow properties of slags formed from the ashes of British coals: Part 2. The crystallizing behaviour of the slags," J. Inst. Fuel 42, 131-4 (1969).

2. Barrick, S. M. and G. F. Moore, "Empirical correlation of coal ash viscosity with ash chemical composition," ASME Paper No. 76-Wa/Fu-3 (1976).

3. Hoy, H. R., A. G. Roberts, and D. M. Wilkins, "Behavior of mineral matter in slagging gasification processes," Publication 672, Instn. Gas Engrs., Nov. 1964. 24 pp.

4. Diehl, E. K., "Viscosity of low-rank coal slags," Proc. Low Rank Coal Technology Development Workshop, San Antonio, TX, June 1981. pp. 5-29 to 5-32.

5. Watt, J. D. and F. Fereday, "The flow properties of slags formed from the ashes of British coals: Part 1. Viscosity of homogeneous liquid slags in relation to slag composition," J. Inst. Fuel $\underline{42}$, 99-103 (1969).

6. Given, P. H., D. Weldon and N. Suhr, "Investigation of the distribution of minerals in coals by normative analysis," The Pennsylvania State University; U. S. DOE Report FE-2494-TR-2, Jan. 1980.

7. Frederikse, H. P. R., T. Negas, and S. J. Schneider, "Development, testing, and evaluation of MHD materials," Contract No. E(49-18)-1230, NBS Quarterly Reports, Nos. 1, 2, 3, 4 (1974) and 5 (1975).

8. Riboud, P. V., Y. Roux, L.-D. Lucas, and H. Gaye, "Improvement of continuous casting powders," Fachberichte Hüttenpraxis Metallweiterverarbeitung $\underline{19}$ (10), 859-66 (1981).

9. Urbain, G., F. Cambier, M. Deletter, and M. R. Anseau, "Viscosity of silicate melts," Trans. J. Br. Ceram. Soc. $\underline{80}$, 139-41 (1981).

Appendix 1. Slag Viscosity/Composition Correlations

A. **Watt-Fereday Correlation**

$$\log \eta = [10^7 m/(t - 150)^2] + c$$

where η = viscosity in poises

t = temperature, °C

$m = 0.00835\ SiO_2 + 0.00601\ Al_2O_3 - 0.109$

$c = 0.0415\ SiO_2 + 0.0192\ Al_2O_3 + 0.0276\ eq.\ Fe_2O_3$
$+ 0.0160\ CaO - 3.92$

$eq.\ Fe_2O_3 = Fe_2O_3 + 1.11\ FeO + 1.43\ Fe$

where slag components are expressed in weight percentages

and, on a weight basis,

$$\Sigma\ SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO = 100\%$$

B. **NBS-Modified Watt-Fereday Correlation**

The equation for $\log \eta$ and units are identical to those above, except that

$$m = 0.0104291\ SiO_2 + 0.0100297\ Al_2O_3 - 0.296285$$

and $c = -0.0154148\ SiO_2 - 0.0388047\ Al_2O_3 - 0.016167\ Fe_2O_3$
$-0.0089096\ CaO - 0.012932\ MgO + 1.04678$

C. **BCURA S^2 Correlation**

$$\log \eta = 4.468\ (S/100)^2 + 1.265\ (10^4/T) - 7.44$$

where η = viscosity in poises

T = temperature, °K

and S = silica ratio = $100\ SiO_2/(SiO_2 + eq.\ Fe_2O_3 + CaO + MgO)$

(slag components expressed in weight percentages)

D. **IRSID Correlation**

$$\eta = AT\ exp(B/T)$$

or $\ln \eta = \ln A + \ln T + B/T$

where η = viscosity in Pa·s (multiply by 10 to convert to poises)

T = temperature, °K

$$\ln A = -19.81 + 1.73 \ (CaO + MnO + MgO + FeO) + 5.82 \ CaF_2$$
$$+ 7.02 \ (Na_2O + K_2O) - 35.76 \ Al_2O_3$$

and $$B = 31,140 - 23,896 \ (CaO + MnO + MgO + FeO) - 46,356 \ CaF_2$$
$$- 39,519 \ (Na_2O + K_2O) + 68,833 \ Al_2O_3$$

Slag components are expressed as mole fractions; for coal ash slags, CaF_2 and MnO can be considered as zero.

E.   Urbain Correlation

$$\eta = AT \ \exp(10^3 B/T)$$

or $\ln \eta = \ln A + \ln T + 10^3 B/T$

where η = viscosity in poises

T = temperature, °K

$\ln A = -(0.2693 \ B + 11.6725)$

and $B = B_0 + B_1 N + B_2 N^2 + B_3 N^3$

where N = mole fraction of SiO_2

and $B_0 = 13.8 + 39.9355 \alpha - 44.049 \alpha^2$

$B_1 = 30.481 - 117.1505 \alpha + 129.9978 \alpha^2$

$B_2 = -40.9429 + 234.0486 \alpha - 300.04 \alpha^2$

$B_3 = 60.7619 - 153.9276 \alpha + 211.1616 \alpha^2$

where $\alpha = CaO/(CaO + Al_2O_3)$

Slag components are expressed as mole fractions. When other minor slag components (modifiers) are present, these are included by redefining α:

$$\alpha^\prime = M/(M + Al_2O_3)$$

where M represents the modifiers as a single mole fraction and is defined as $M = \Sigma M_i L_i$ where M_i's are the individual mole fractions and L_i is the number of oxygen atoms in the molecule. Thus, for the slags considered in these studies containing CaO, MgO, Na_2O, K_2O, FeO, TiO_2, and (occasionally) SO_3,

$$M = CaO + MgO + Na_2O + K_2O + FeO + 2 \ TiO_2 + 3 \ SO_3$$

(again, all components expressed as mole fractions).
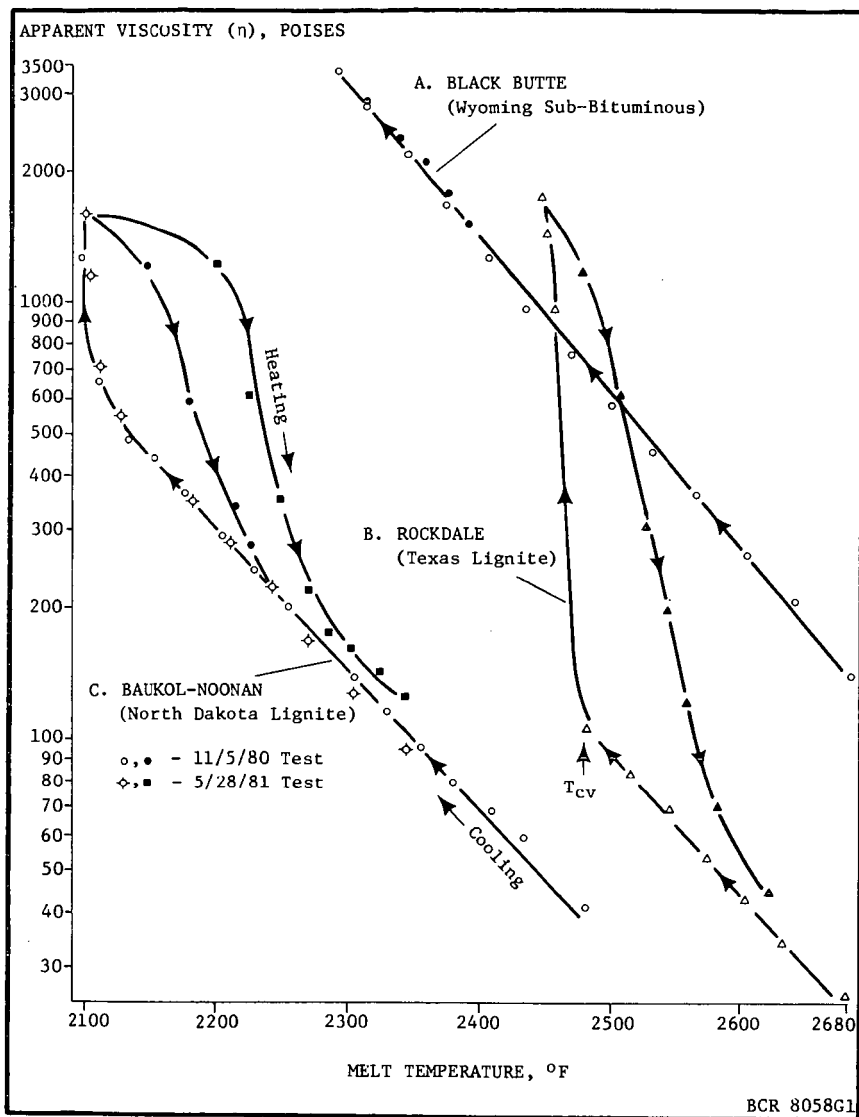
Figure 1. Representative Slag Viscosity Curves for Three Western U.S.
Low-Rank Coals

APPARENT VISCOSITY (n), POISES

ASH COMPOSITION, WT. PERCENT

	BIG BROWN	MARTIN LAKE
SiO_2	40.6	38.6
Al_2O_3	14.5	13.6
Fe_2O_3	7.9	9.1
TiO_2	1.2	1.1
CaO	13.2	11.3
MgO	3.8	4.6
Na_2O	0.6	2.1
K_2O	0.7	0.8
SO_3	16.8	18.1

ASH FUSIBILITY, F

I.D.	2080	2100
S.T.	2120	2140
F.T.	2180	2200

MARTIN LAKE-EXPERIMENTAL

BIG BROWN-THEORETICAL

MARTIN LAKE-THEORETICAL

BIG BROWN-EXPERIMENTAL
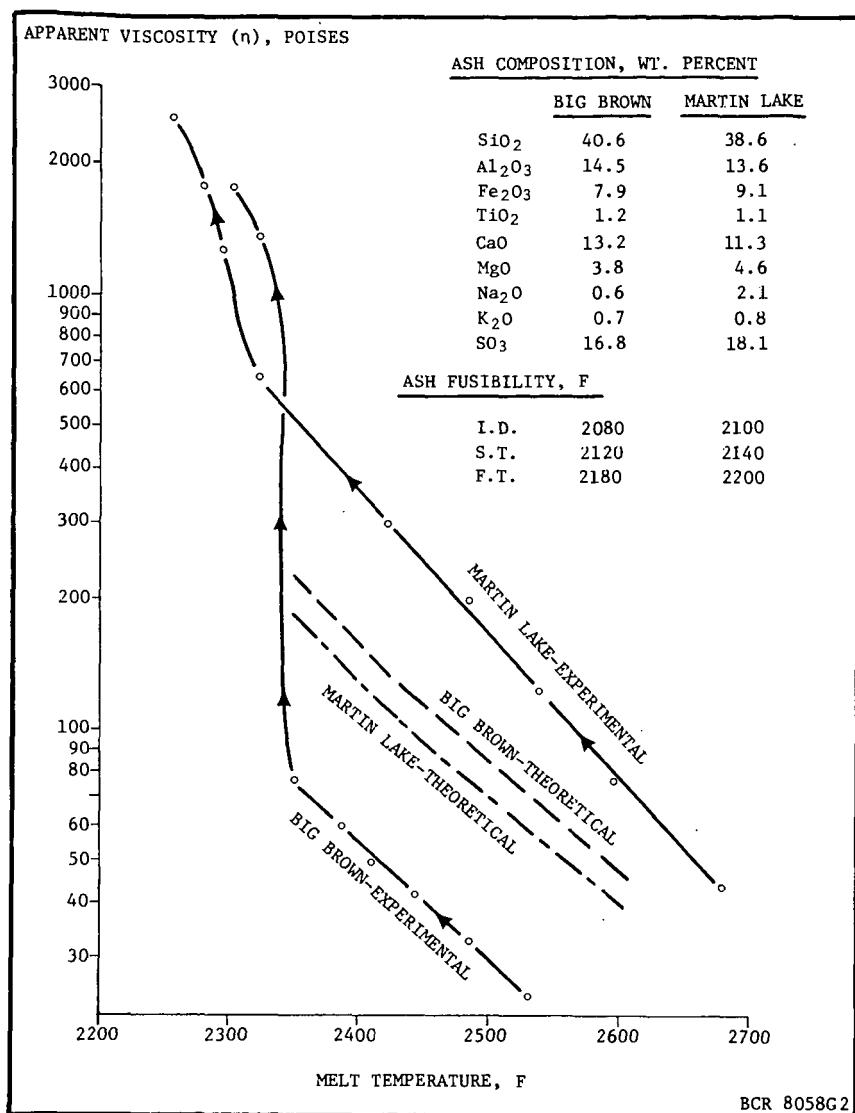
MELT TEMPERATURE, F

BCR 8058G2

Figure 2. Comparison of Predicted (Watt-Fereday) and Actual Slag Viscosity
Curves for Two Texas Lignites

195